



TITLE:

<Division of Multidisciplinary Chemistry>Molecular Rheology

AUTHOR(S):

CITATION:

<Division of Multidisciplinary Chemistry>Molecular Rheology. ICR Annual Report 2011, 18: 38-39

ISSUE DATE:

2011

URL:

<http://hdl.handle.net/2433/154956>

RIGHT:

Division of Multidisciplinary Chemistry – Molecular Rheology –

<http://rheology.minority.jp/en/>



Prof

WATANABE, Hiroshi
(D Sc)



Assoc Prof

MASUBUCHI, Yuichi
(D Eng)



Assist Prof

MATSUMIYA, Yumi
(D Eng)



Program-Specific Assist Prof

UNEYAMA, Takashi
(D Sc)



Techn*

OKADA, Shinichi

* Re-employed Staff



PD

CHEN, Quan
(Ph D)

Students

SUZUKI, Shin-ya (D3)
TAKADA, Jyun (D1)
SUMIDA, Koji (M2)
KAWASAKI, Yohji (M2)

KITANO, Jun-ya (M2)
YAMAMOTO, Satoshi (M1)
TACHIIRI, Akihiro (M1)
KURITA, Yushi (M1)

HORIUCHI, Saki (UG)
YOSHIZAWA, Hiroki (UG)

Visitors

Prof KWON, Youngdon
Prof THEODOROU, Doros
Prof MÜLLER-PLATHE, Florian
Mr UNIDAD, Herwin Jerome

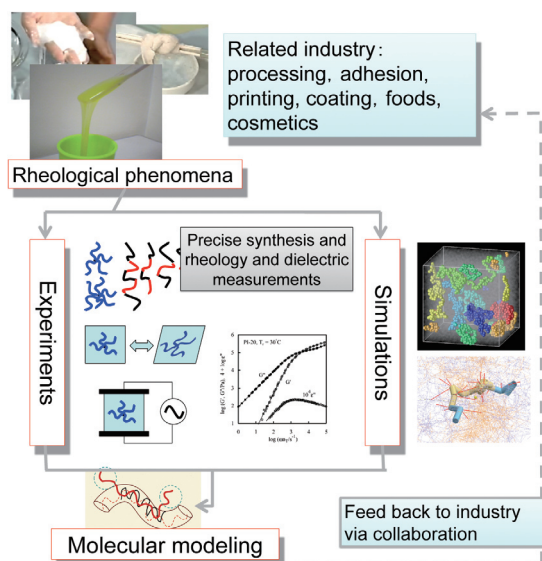
Sungkyunkwan University, Korea, R., 1 April–30 September
Technical University of Athens, Greek, 7–12 September
Technische Universität Darmstadt, Germany, 23 September
University of Naples, Italy, 18 March–27 April

Scope of Research

The molecular origin of various rheological properties of material is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluid while heterogeneous polymeric systems exhibit plasticity in addition to these features. For basic understanding of the features, the molecular motion and structures at various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of auto-correlation of the orientation with dynamic dielectric spectroscopy. Direct observation of molecular motion is also carried out with fluorescent microscopy and molecular simulations.

KEYWORDS

Rheology Polymers Suspensions
Softmatters Emulsions



Selected Publications

- Watanabe, H.; Chen, Q.; Kawasaki, Y.; Matsumiya, Y.; Inoue, T.; Urakawa, O., Entanglement Dynamics in Miscible Polyisoprene/Poly(p-tert-butylstyrene) Blends, *Macromolecules*, **44**(6), 1570-1584 (2011).
- Matsumiya, Y.; Uno, A.; Watanabe, H.; Inoue, T.; Urakawa, O., Dielectric and Viscoelastic Investigation of Segmental Dynamics of Polystyrene above Glass Transition Temperature: Cooperative Sequence Length and Relaxation Mode Distribution, *Macromolecules*, **44**(11), 4355-4365 (2011).
- Uneyama, T.; Horio, K.; Watanabe, H., Anisotropic Mobility Model for Polymers under Shear and Its Linear Response Functions, *Phys. Rev. E*, **83**(6), 061802 (2011).
- Masubuchi, Y.; Yaoita, T.; Matsumiya, Y.; Watanabe, H., Primitive Chain Network Simulations for Asymmetric Star Polymers, *J. Chem. Phys.*, **134**, [194905-1]-[194905-7] (2011).
- Watanabe, H., Slow Dynamics in Homopolymer Liquids, *Polym. J.*, **41**(11), 929-950 (2009).

Dielectric and Viscoelastic Investigation of Segmental Dynamics of Polystyrene above Glass Transition Temperature: Cooperative Sequence Length and Relaxation Mode Distribution

Atactic polystyrene (PS) has the type-B dipole perpendicular to the chain backbone so that its segmental motion activates the dielectric relaxation. For monodisperse PS and oligostyrene (OS) samples of various molecular weights M , details of this motion were examined at temperatures T well above T_g through comparison of the complex modulus, $G^*=G'+iG''$, and the complex dielectric permittivity, $\epsilon^*=\epsilon'-i\epsilon''$, measured as functions of the angular frequency ω . For the OS samples, $G^*(\omega)$ and $\epsilon^*(\omega)$ fully relaxed through the segmental dynamics thereby exhibiting low- ω terminal tails, $G'(\omega)\propto\omega^2$, $G''(\omega)\propto\omega$, $\Delta\epsilon'(\omega)\equiv\epsilon'(0)-\epsilon'(\omega)\propto\omega^2$, and $\epsilon''(\omega)\propto\omega$, at ω below the segmental relaxation frequency ω_s . For the PS samples, $G^*(\omega)$ relaxed partly through the segmental dynamics and then exhibited the polymeric full relaxation characterized by the Rouse-like behavior followed by the terminal flow behavior (with/without intermediate entanglement plateau depending on M). In contrast, $\epsilon^*(\omega)$ of the PS samples still relaxed completely through the segmental dynamics. For respective samples, the $G^*(\omega)$ and $\epsilon^*(\omega)$ data in the segmental

relaxation zone exhibited very similar relaxation mode distribution. Nevertheless, a ratio of the dielectrically and viscoelastically detected segmental relaxation times, $r(M)=\omega_{s,G}/\omega_{s,\epsilon}$, and the dielectric relaxation intensity, $\Delta\epsilon(M)$, decreased with increasing M up to $M^*\cong 2\times 10^3$ and then became insensitive to M on a further increase of M . The viscoelastic segmental relaxation reflects the cooperative torsion of the repeating units along the molecular backbone, while the dielectric segmental relaxation detects reorientational motion of those units affected by both intra- and inter-molecular cooperativity. The observed decreases of $r(M)$ and $\Delta\epsilon(M)$ suggested that the dimension ζ_m of the whole OS molecule (over which the cooperative torsion occurs) is smaller than the length scale ζ_c for the inter-molecular cooperative motion and that ζ_m approaches ζ_c on an increase of M up to M^* . Consequently, the high- M PS molecules having $\zeta_m>\zeta_c$ exhibited the M -insensitive $r(M)$ and $\Delta\epsilon(M)$. Thus, the M value for the crossover between these two regimes, $M^*\cong 2\times 10^3$, can be taken as the molecular weight of the cooperative sequence along the PS backbone. Furthermore, the quantitative similarity of the viscoelastic and dielectric mode distributions suggests that the cooperative torsion of the repeating units along the molecular backbone is governed by the cross-correlation of the units belonging to different molecules.

